

Electrolyte for the Galvanic Deposition of Aluminum-Magnesium Alloys

[0001] The invention is directed to an electrolyte for the galvanic deposition of aluminum-magnesium alloys, said electrolyte containing at least one organoaluminum complex compound and an alkylmagnesium compound. The invention is also directed to a method for producing said electrolyte, to a coating method, to the use of the electrolyte, and to an electrolysis kit.

[0002] Recently, magnesium-aluminum-organic complex compounds have been used for the electrolytic deposition of aluminum-magnesium alloys, and this has been described in WO 00/32847 A1. There has been rapidly increasing interest in electrolytic coating of metallic workpieces with aluminum-magnesium alloys because of the excellent corrosion protection as a result of the aluminum-magnesium layers and because of the ecological safety thereof. Therefore, electroplating using magnesium-aluminum-organic electrolytes operating at temperatures ranging from 60 to 150°C in closed systems has gained major technical importance.

[0003] WO 00/32847 A1 suggests complex compounds of the general type $MAIR_4$ and mixtures thereof in combination with aluminum alkyls AlR_3 as particularly suitable electrolytes. They are used in the form of solutions in liquid, aromatic hydrocarbons. M can be an alkali metal such as sodium, potassium, rubidium and cesium, R represents alkyl residues with preferably one, two or four carbon atoms.

[0004] However, the use of such electrolyte systems has crucial disadvantages. The systems known to date involve the characteristic feature that, initially, the required organomagnesium complex compounds are not present in the electrolyte, and complex *in situ* electrochemical production thereof is required at

that point in time when it comes to using the electrolyte. Thus, ready-for-use starting mixtures exclusively contain organic aluminum compounds, but no magnesium compounds. For example, typical compositions of such starting mixtures include molar ratios of from 1:0.1 to 0.1:1 of M^1AlR_4 to M^2AlR_4 , wherein M^1 is different from M^2 and is Na, K, Rb, Cs, particularly Na, K. The molar ratios of all components $AlR_3/(M^1AlR_4 + M^2AlR_4)$ /aromatic hydrocarbon ranges from 1:0.1:1 to 1:2:10, particularly from 1:1:3 to 1:1:5.

[0005] In such electrolytes the above-mentioned starting electrolyte free of magnesium is initially placed in electrolytic cells suitable for coating. Thereafter, the required organic magnesium complex is electrochemically generated *in situ* by applying a current, using separate aluminum and magnesium anodes or an aluminum-magnesium mixed electrode, until the concentration of magnesium complex required for coating is achieved in the electrolyte.

[0006] Moreover, deposition of aluminum-magnesium layers already takes place in the system before that point in time, i.e., before reaching the necessary concentration of magnesium complex, which is undesirable because these layers do not have the proper composition of Al and Mg. For this reason, dummy metal sheets must be placed in the system in order to collect the deposited aluminum-magnesium layers. Deposition on dummy metal sheets proceeds until the required concentration of aluminum-magnesium complexes is reached. Thereafter, the dummy metal sheets are removed, and the desired layers having the desired aluminum-magnesium composition, e.g. Al:Mg = 75:25 mole-%, are deposited on the substrate. The dummy metal sheets must be either discarded or subjected to complex cleaning for further use.

[0007] From the description given above, it can easily be seen that this process is highly complex, requiring a long pre-run time until the corresponding desired aluminum-magnesium concentrations are obtained. Furthermore, mounting, removing and cleaning the dummy metal sheets used arises as additional

working step. For this reason, the electrolyte solutions identified as particularly effective in WO 00/32847 A1 can only be employed via the above-described electrochemical production of organomagnesium complexes in a conditioning phase preceding the actual coating, with all the disadvantages mentioned above.

[0008] Furthermore, direct addition of a corresponding magnesium compound to the electrolyte is well-known from the WO 00/32847 A1 prior art, allowing to omit the above-mentioned conditioning phase. Here, a magnesium-aluminum alkyl complex, $\text{Mg}[\text{Al}(\text{Et})_4]_2$, is employed in the electrolyte. While this method can be performed on a laboratory scale, it involves the drawback that it cannot be performed on an industrial scale because the above complex is not industrially available, and the production thereof is highly complex and costly.

[0009] Appropriate electrolytes for an industrial process for the coating of substrates with Al-Mg alloys, which could be carried out economically and effectively, are not known to date. Further development of electrolytes for the galvanic deposition of aluminum-magnesium alloys are of great technical importance and highly interesting in economical and ecological terms.

[0010] The technical object of the invention is therefore to provide an electrolyte which can be produced in a preferably simple, efficient fashion and at low cost, which allows commercial introduction of the aluminum-magnesium coating process and avoids the need of the above-mentioned conditioning phase to form organic Mg complexes.

[0011] The above technical object is accomplished by means of an electrolyte for the galvanic deposition of aluminum-magnesium alloys, containing at least one organoaluminum complex compound of formula MAIR_4 or mixtures thereof and an alkylmagnesium compound, in which formula M represents sodium, potassium, rubidium or cesium, and R represents a $\text{C}_1\text{-C}_{10}$ alkyl group,

preferably a C₁-C₄ alkyl group. In a particularly preferred embodiment the electrolyte additionally includes a trialkylaluminum compound.

[0012] In a particularly preferred fashion, an electrolyte is used which includes AlR₃, M¹AlR₄, M²AlR₄ and Mg(R¹)_x(R²)_y, wherein M¹ and M² are different from each other, representing Na, K, Rb or Cs, R represents a C₁-C₁₀ alkyl group, preferably a C₁-C₄ alkyl group, R¹ and R² independently represent a C₁-C₂₀, preferably a C₂-C₁₀ alkyl group, and x = 0 to 2, and y = 0 to 2, and x + y = 2.

[0013] Surprisingly, it was found that the electrolyte of the invention can be used in the coating of materials with aluminum-magnesium alloys, without requiring *in situ* production of organomagnesium complexes in a time- and cost-intensive conditioning phase prior to the actual coating process.

[0014] In a preferred fashion the alkylmagnesium compound is included in the electrolyte in an amount of from 0.01 to 10 mole-%, preferably from 0.1 to 1 mole-%, relative to the aluminum complex. Particularly preferred alkylmagnesium compounds used in the electrolyte are selected from the group of Mgbutyl_{1.5}octyl_{0.5}, Mgbutyl_{1.0}ethyl_{1.0}, Mgsec-butyl_{1.0}n-butyl_{1.0} or mixtures thereof.

[0015] The organoaluminum complex compound and the alkylmagnesium compound can preferably be present in an organic solvent. In a particularly preferred fashion the organic solvent is an aromatic solvent, in which case solvents such as benzene, toluene or xylene or mixtures thereof can be used.

[0016] Compared to the above-mentioned magnesium-aluminum ethyl complexes Mg[Al(Et)₄]₂, the alkylmagnesium compounds specified above have the advantage of being industrially available and allowing easy and low-cost production. The production of the electrolyte proceeds according to the following

steps. Initially, the organoaluminum complex compound of formula $MAIR_4$ or a mixture thereof, optionally in combination with trialkylaluminum, is supplied. This is followed by addition of an alkylmagnesium compound as described above. M and R have the same meanings as described above. Metering of the alkylmagnesium compound during production of the electrolyte has the advantage that the required concentration of magnesium and aluminum can be adjusted directly, making it possible to do completely without the conditioning process specified above. Furthermore, it is possible to add the alkylmagnesium compound even during the coating process in order to maintain the appropriate magnesium concentration which is desired and required for coating.

[0017] In a particularly preferred embodiment the alkylmagnesium compound is a mixed alkylmagnesium compound of formula $Mg(R^1)_x(R^2)_y$, wherein R^1 and R^2 independently represent a C_1 - C_{20} , preferably a C_2 - C_{10} alkyl group, and $x = 0$ to 2 , and $y = 0$ to 2 , and $x + y = 2$. In a particularly preferred embodiment the alkylmagnesium compounds are added dissolved in a hydrocarbon, and the alkylaluminum complexes are supplied dissolved in an aromatic hydrocarbon. The hydrocarbon for the aluminum compound is selected from the group of i-pentane, n-pentane, hexane, n-hexane, heptane, n-heptane, toluene and xylene.

[0018] Using the electrolyte according to the invention, aluminum-magnesium layers of varying concentration sequences of aluminum and magnesium can be produced in a single operation by simple and free selection of the added quantity of organomagnesium compounds. The appropriate concentration of aluminum-magnesium is adjusted via the added amount of organomagnesium compound. The electrolyte according to the invention also has the advantage of good conductivity and throwing power

[0019] The electrolyte according to the invention allows operation with indifferent anodes used in coating parts of geometrically complicated shape. In-

different electrodes are those not undergoing dissolution during the coating process, i.e., not consisting of Al or Mg or alloys thereof. When coating with indifferent electrodes, organomagnesium and organoaluminum compounds must therefore be metered into the electrolyte solution. The appropriate concentration of aluminum-magnesium is adjusted via the added amount of organomagnesium compounds and organoaluminum compounds. According to the previous state of the art, working with indifferent anodes in *in situ* production of organomagnesium complexes has been excluded, in principle, which also applies to the production of layers of varying aluminum-magnesium composition in a single operation. This is not possible either in the above-described *in situ* process using a conditioning step to furnish the magnesium concentration in the electrolyte.

[0020] The invention is also directed to an electrolysis kit for the galvanic deposition of aluminum-magnesium alloys on electrically conducting materials or electrically conducting layers, including:

- a) the organoaluminum complex compounds described above, or alkylaluminum compounds of claims 1 to 3 and 1, 3, 5, 6; and
- b) an alkylmagnesium compound in accordance with claims 1, 3, 5, 6.

[0021] In a preferred embodiment the compounds a) and b) are dissolved in an organic solvent.

[0022] The invention is also directed to a method of coating electrically conducting materials or layers with aluminum-magnesium alloys using the electrolyte in accordance with claims 1 to 9, in which method the alkylmagnesium compound in accordance with claims 1, 3, 5 and 6 is metered in the desired amount during the coating phase in order to obtain or maintain a desired concentration of magnesium and aluminum.

[0023] The invention is also directed to the use of the electrolyte according to the invention for the production of layers of aluminum alloys on electrically conducting materials or electrically conducting layers.

[0024] The invention will be illustrated in more detail with reference to the examples below.

Example 1

Use of Mgbutyl_{1.5}octyl_{0.5}, 20% in heptane (product BOMAG[®] from the company Crompton)

[0025] The entire implementation of the reaction was under argon protective gas.

[0026] Step 1: Following removal of heptane by condensation, the BOMAG[®]/heptane solution was adjusted to a content of 0.32 mmol/g using toluene.

[0027] Step 2: 55.4 g of an electrolyte having the following composition: 0.8 K[Al(Et)₄] + 0.2 Na[Al(Et)₄] + 1.17 Al(Et)₃ + 3.85 toluene was added with 2.85 g of BOMAG/toluene solution (about 1.0 mole-%, relative to the electrolyte formulation).

[0028] About 58 g of an electrolyte was obtained.

Coating test

[0029] General conditions:

[0030] All deposition tests were performed under standard conditions. The magnesium component was directly pipetted into the electrolyte.

Anode material: 2 alloy electrodes, AlMg, $25.55 \times 10 \times 5$ mm
Cathode: hexagonal screw, 8.8, M8 \times 25
Cathode pretreatment: degreasing, descaling in ultrasonic bath with 8% HCl, H₂O wash, vacuum drying, storage under argon
Cathode immersion depth: complete
Cathode rotation: 60 rpm
Distance to anode: 10 mm
Effective cathode surface: about 10 cm²
Bath agitation: 2 cm magnet in glass jacket, 250 rpm
Bath temperature: 94-98°C

[0031] Deposition was started at a current density of 0.05 A/dm². After a few minutes, a bright overlay could be seen on the parts to be coated. The current density was gradually raised to 3.0 A/dm². Deposition was terminated after a current quantity of 1.499 mF, corresponding to a layer thickness of 5 μ m. The layer is bright and silvery.

RF analysis of the layer: 26.79 wt.-% Mg, 73.21 wt.-% Al

Example 2

Use of Mgethyl_{1.0}butyl_{1.0}, 20% in heptane (BEM, company Akzo-Nobel)

[0032] The reaction was effected under argon protective gas.

[0033] Step 1: Following removal of heptane by condensation, the BEM/heptane solution was adjusted to a content of 0.41 mmol/g using toluene.

[0034] Step 2: 60.6 g of an electrolyte having the following composition: 0.8 K[Al(Et)₄] + 0.2 Na[Al(Et)₄] + 1.17 Al(Et)₃ + 3.85 toluene was added with 2.0 ml of BEM/toluene solution (about 0.9 mole-%, relative to the electrolyte formulation). About 62 g of an electrolyte was obtained.

Coating test:

[0035] The deposition conditions were as in Example 1. Deposition was started directly with a current density of 2.0 A/dm² which remained unchanged during the entire electrolysis. There was an instantaneous bright deposition of Al/Mg. Deposition was terminated after a current quantity of 3.38 mF, corresponding to a layer thickness of 11 µm. An excellent, highly uniform, silvery layer with no recognizable flaws was obtained.

RF analysis of the layer: 26.78 wt.-% Mg, 73.22 wt.-% Al

Example 3

Use of Mgethyl_{1,0}butyl_{1,0}, 20% in isopentane (BEM from the company Albe-marle)

[0036] The reaction was effected under argon as protective gas.

[0037] Step 1: The BEM/isopentane solution with a content of 1.85 mmol/g Mg component is used without further pretreatment.

[0038] Step 2: 70.04 g of an electrolyte having the following composition: 0.85 K[Al(Et)₄] + 0.15 Na[Al(Et)₄] + 1.08 Al(Et)₃ + 3.15 toluene was added

with 0.5 g of BEM/isopentane solution (about 0.8 mole-%, relative to the electrolyte formulation).

Coating test

[0039] The deposition conditions were as described in Example 1. Deposition was effected at a current density of 1.0 to 3.0 A/dm². Deposition was terminated after a current quantity of 6.8 mF, corresponding to a layer thickness of 20 µm. A highly uniform, silvery layer was obtained.

RF analysis of the layer: 41.4% Mg, 58.9% Al

Comparative Example 1

Use of electrolytes from the company Albemarle for Al-Mg deposition, but without direct addition of Mg-alkyl solution (conditioning electrolyte)

[0040] 65.0 g of an electrolyte having the following composition: 0.8 K[Al(Et)₄] + 0.2 Na[Al(Et)₄] + 1.17 Al(Et)₃ + 3.85 toluene was used with preparatory conditioning under the general conditions as described above, but without previous addition of Mg-alkyl solution, so that, as required in accordance with the previous state of the art, the Mg complex compound has to be generated electrochemically in a conditioning phase before the electrolyte is ready for use in the deposition of Al-Mg alloys.

[0041] Conditioning step 1: Starting with an initial current density of 0.05 A/dm², electrolysis was effected with the current density increasing up to the maximum possible value of 1.0 A/dm². After a current quantity of 7.20 mF, with poor throwing power, a dull, gray coating was obtained.

[0042] Conditioning step 2: After replacing the cathode, conditioning was continued at 1.0 to 1.2 A/dm². After a current quantity of 7.24 mF, with scarcely improved throwing power, a markedly brighter layer faintly lustrous in parts was obtained.

[0043] Conditioning step 3: Again, after replacing the cathode, but now with a significant increase of the maximum allowable current density of 1.23 beyond 1.5 and up to 2.0 A/dm², a uniform lustrous coating with significantly improved throwing power was obtained. The amount of current used was 4.96 mF.

[0044] Conditioning step 4: Reaching the final condition, a lustrous coating was obtained using a current density of 3.0 A/dm², with throwing power unchanged compared to step 3. The current quantity was 3.73 mF.

[0045] The electrolyte is conditioned and operational only after this procedure.